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13. ABSTRACT *(Maximum 200 words)*

The reserach project involves two interrelated areas of investigation which are directed toward obtaining a fundamental understanding of the interrelationships between the structure and mechanical function of the collagen network of intestine. The approach is soundly based on knowledge gained over the past 10 years in the study of tendon. Current studies of the hierarchical organization of intestinal collagen were extended in order to develop mechanical models which consider the actual multicomposite structure of the structural protein. This approach led to an understanding of the age-dependence of mechanical properties and of structural changes at the various levels of organization. A comparison of different tissues which function under a variety of stress conditions is extremely important for developing a fundamental understanding of the relationships between the organization of structural proteins.

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In liquid crystalline systems the focal point was to establish the relationships between solid state organization and mechanical behavior. This included studying the energy absorbing mechanisms during irreversible deformation in these anisotropic layered structures since unusually high toughness has been observed at cryogenic temperatures and very high rates of loading(even under ballistic impact). In collaboration with the Celanese Corporation, researchers systematically varied the hierarchical layered structure which allowed the correlation with the observed mechanical behavior.

HIERARCHICAL STRUCTURE IN POLYMERIC SOLID
AND ITS INFLUENCE ON PROPERTIES

FINAL REPORT

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JUNE 10, 1992

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A. Statement of Problem Studied

A-1. Biological Systems

The research project involves two interrelated areas of investigation which are directed toward obtaining a fundamental understanding of the interrelationships between the structure and mechanical function of the collagen network of intestine. Our approach is soundly based on knowledge gained over the past 10 years in the study of tendon. We propose to extended our current studies of the hierarchical organization of intestinal collagen in order to develop mechanical models which consider the actual multicomposite structure of the structural protein. Our approach led to an understanding of the age-dependency of mechanical properties and of structural changes at the various levels of organization. A comparison of different tissues which function under a variety of stress conditions is extremely important for developing a fundamental understanding of the relationships between the organization of structural proteins.

1. Elucidated the hierarchical organization of collagen in intestine from the microfibril level to the level of the fibrous entities observed in the optical microscope.

2. Analyzed the age-dependency of the structure at each level of organization and the nature of interactions between hierarchical levels.

3. Determined the mechanical behavior of intestine including the unusual and highly interesting anisotropic properties.

4. Developed mechanical models of the multicomposite biaxial system which will include the effects of aging.

5. Compared intestine with the tendon and other tissues in terms of age-dependency of the interrelationships among collagen compostion, hierarchical composite structure, and mechanical behavior.

A-2. Liquid Crystalline Systems

The focal point was to establish the relationships between solid state organization and mechanical behavior. We are particularly intested in studying the energy absorbing mechanisms during irreversible deformation in these anisotropic layered structures since unusually high toughness has been observed at cryogenic temperatures and very high rates of loading(even under ballistic impact). In collaboration with the Celanese Corporation, we systematically varied the hierarchical layered structure which allowed the correlation with the observed mechanical behavior.

1. Determined the hierarchiacal organization of various thermotropic liquid crystalline polyesters (LCP) from the molecular level to the 'macro' scale.

2. Analyzed the interactions between levels via 'tie' fibers.

3. Measured the reversible and irreversible mechanical behavior with particular emphasis on the nature of anisotropic properties.

4. Developed mechanical modes that will accurately describe the anisotropic structures.

5. Compared these synthetic systems with the anisotropic biological systems in connective tissue.

B. Summary of Results

B-1. Lessons from Nature

Optical microscope techniques are used to characterize the hierachical structure of the collagenous components of the human intervertebral disc. In the anterior annulus fibrosus, the thickness of the lamellae increases abruptly 2 mm inward from the edge of the disc dividing the annulus into peripheral and transitional regions. Lamellae in the lateral and posterior aspects of the disc have a broad distribution of lamellar thickness throughout the annulus. In alternating lamellae, fibers are inclined with respect to the vertical axis of the spine in a layup structure. From the edge of the disc inward to the nucleus, this interlamellar angle decreases from +62 to +45 degrees. Within lamellae, the collagen fibers exhibit a planar crimped morphology. The plane of the waveform is inclined with respect to the vertical axis by the interlamellar angle. From the edge of the disc inward, the crimp angle increases from 20 to 45 degrees and the crimp period decreases from 26 to 20 μm. A hierarchical model of the intervertebral disc has been developed that incorporates these morphological gradients.

The time-dependent mechanical response of the canine intervertebral disc in axial compression is related to the response of the various levels of the hierarchical organization. In stress relaxation the initial transverse bulging of the disc recovers almost completely with time. The corresponding decrease in volume correlates with the measured loss of water from the disc. The three-dimensional architecture of the disc, examined by sectioning isolated discs that had been fixed in compression, accommodates the volume displacement. Bulging of the peripheral lamellae is minimized by the curvature of the vertebral interface and by stress-driven transport of water out of the disc through the cartilage end-plates into the vertebral bodies. Even though the disc undergoes macroscopic compression, the fibers of the lamellae are loaded in tension and their mode of deformation is compared with that of other connective tissues such as tendon and intestine.

Time-dependence in the mechanical response of the intervertebral disc has previously been shown to arise from the transport of water out of the disc. A creep model has been devised which describes the water transport in terms of the disc structure. This model assumes that the flow of water is the result of a pressure gradient across the cartilage end-plates, caused by an externally applied stress. The fluid transport properties of the

cartilage determine the flow rate. Several cases are studied; those that best fit the experimental results use either a strain-dependent or a time- and strain dependent pressure gradient. The permeability of the disc system is in the range (0.20 to 0.85) x 10^{-17} m^4 N^{-1} sec^{-1} and depends on the stress level. These values are lower than those reported in the literature for articular cartilage, but this can be explained in part by the differences in water content of the cartilage types. Permeability is found to decrease with applied stress, and both the strain- and time- dependence parameters increaes in magnitude with stress. It can be shown that the analytical models of the creep response of the disc are analogous to three- and four- parameter viscoelastic models that employ springs and dashpots.

Hierarchial structure in biocomposite systems such as in collagenous connective tissue have many scales or levels, have highly specific interactions between these levels, and have the architecture to accomodate a complex spectrum of property requirements. As examples, the hierarchical structure-property relationships are described in three soft connective tissues; tendon, intestine and intervetebral disc. In all instances, we observed numerous levels of organization with highly specific interconnectivity and with unique architectures that are designed to give the required spectrum of properties for each oriented composite system. From these lessons in biology, the laws of complex composite systems for functional macromolecular assemblies are considered. Finally, demonstrations of the application of these laws to simple synthetic composites are given including continuous multilayered polymeric materials, liquid cystalline polymers and " hard elastic" membranes. It is shown that structure-property relationships can only be described, and in some instances predicted, if these complex synthetic materials are accurately defined in terms of their hierarchial structure.

B-2. Acoustic Analysis of Damage in LCP Composites

Damage processes during cyclic deformation of short glass fiber reinforced liquid crystalline polyester (LCP) have been investigated by acoustic emission (AE) source location techniques. The approach consisted of placing two sensors equidistant from a notch and monitoring the AE signals emitted from the damage accumulation as cycling progressed. This was done in conjunction with a video- camera recording systems and an infra-red thermal measuring device. The visual and thermal data indicated that no measurable stable crack propagation occurred. Acoustic emission measurements suggested that failure resulted in the last 20 % of the cycling time by a damage-related microcracking

mechanism. *Three-dimensional linear location plots showed that damage was very* localized in the notch region in the reinforced materials and somewhat broader in the neat LCP resin. Correlations between the location of damage, the time and stress level at which it occurred as well as its AE amplitude characteristics have been made.

B-3. Morphology and Mechanical Properties of LCP/ PET Blends

The structural hierarchy in injection molded blends of poly(ethylene terephthalate) (PET) and a commercial liquid crystal polymer (LCP), two immiscible polymers, was characterized at various blends compositions. The macroscopic core and skin have a gradient structure and are subdivided into ordered and disordered layers. The sublayres consist of rodlike domains at 25% LCP. The domains become thinner, longer, and more fibril-like with increasing LCP concentration. The interconnection between the LCP domains also becomes more significant at higher LCP concentrations. The highest degree of orientation in the injection direction is at the mold surface and the lowest at the sample center. The LCP orientation reflects the elongational and fountain flow in the mold and increases with increasing LCP concentration. Schematic structural models were used to illustrate the levels of structure in these blends. A minimum exists in the tensile strength, elongation at break, and impact strength with varying blend composition at approximately 50% LCP. The tensile strength of the LCP-rich blends is significantly lowered by the presence of a weldline or an angle between the stress and orientation directions. The unique mechanical properties of the LCP depend on the formation of a highly oriented and highly connected hierarchical structure that does not exist in blends with 75% or less LCP.

The domain morphology and mechanical properties of fibers spun from blends of a thermotropic liquid cystalline polymer, Vectra A-900, and poly(ethylene terephthalate) (PET) have been studied across the entire compostion range. The PET phase was removed by etching to reveal fibrillar LCP domains in the blends of all compostions. The 0.5 μm fibril appeared to be the basic structural entity of the LCP domains. A primary effect of compostion was the change from discontinuous fibrils when the composition was 35 and 60% by weight LCP to continuous fibrills when the composition was 85 and 96% LCP. This transition had major ramifications on the mechanical properties: the modulus increased abrubtly between 60 and 85% LCP, and a change in the fracture mode from brittle fracture to a splitting mode was accompanied by an increase in fracture strength. Different models were required to describe the mechanical properties of the discontinuous and continuous fibril morphologies. Analytic models for the short aligned fibers of Nielsen, and Kelly and

Tyson were applicable when the LCP fibrils were discontinuous, while modulus and strength of blend fibers with continuous LCP fibrils were described by the rule of mixtues.

B-4. Damage Zone in Notched PP

The irreversible deformation behaviour of polypropylene during sharp single-notched tension testing has been studied as a function of temperature. Specimens were tested at room temperature, -20, -40, and -60°C with photographs taken of the notch tip area during testing. Below T_g, a narrow wedge-shaped damage zone grew from the notch tip with increased stress. The damage zone length correlated with the ratio of applied stress to yield stress in agreement with the dugdale model. The crack tip opening displacement (CTOD) was found to follow the predicted Dugdale CTOD when modified by using the secant modulus to account for viscoelasticity. The shape of the damage zone did not agree with the Dugdale model near the notch tip, but instead was found to follow a path of the minor principal stress trajectory. Above T_g, the damage zone had a lower length-to-width ratio which no longer resembled the Dugdale model.

B-5. Ductility of Filled Polymers

The ductility of a calcium carbonate filled amorphous copolyester PETG in uniaxial tensile test was examined as a function of the filler volume fraction. A ductile-to-quasibrittle transition occurred as the volume fraction of filler increased. This transition was from propagation of a stable neck through the entire gauge length of the sample to fracture in the neck without propagation. The draw stress (lower yield stress) did not depend on the filler content and was equal to the draw stress of the unfilled polymer. It was therefore possible to use a simple model to predict the dependence of the fracture strain on the filler volume fraction. When the fracture strain decreases to the draw ratio of the polymer, the failure mechanism changes, and the fracture strain drops sharply. The critical filler content at which the fracture mode changes is determined primarily by the degree of strain-hardening of the polymer.

C. List of All Publications and Technical Reports

1. J.J. Cassidy, A. Hiltner, E. Baer, "Hierarchial Structure of the Intervertebral Disc", Connective Tissue Research, 23, 75, (1989).

2. J.J. Cassidy, A. Hiltner, E. Baer, "The Response of Hierarchical Structure of the Intervertebral Disc to Uniaxial Compression", J. Materials Science: Materials in Medicine, 1,69, (1990) .

3. J.J. Cassidy, M.S. Silverstein, A. Hiltner, E. Baer, "A Water Transport Model for the Creep Response of the Intervertebral Disc", J. Materials Science: Materials in Medicine, 1, 81, (1990).

4. E. Baer, J.J. Cassidy, A. Hiltner, "Hierarchical Structure of Collagen Composite System: Lessons from Biology", Pure and Applied Chemistrtry, 63 (7), 961 (1991).

5. T. Weng, A. Hiltner , E. Baer, "Damage Analysis in Reinforced LCP Composites by Acoustic Emission Location Techniques", J. Composite Materials, 24, 103, (1990).

6. M.S. Silverstein, A. Hiltner, E. Baer, "Hierarchical Structure in LCP/PET Blends", J. Applied Polymer Science, 43, 157, (1991).

7. J.X. Li, M.S. Silverstein, A. Hiltner, E. Baer, "Morphology and Mechanical Properties of Fibers from Blends of a Liquid Crystalline Polymer and Poly(ethylene terephthalate)", J. Applied Polymer Science, 44, 1531, (1992).

8. J. Snyder, A. Hiltner, E. Baer, "Analysis of the Wedge-Shaped Damage Zone in Edge-Notched Polypropylene", J. Materials Science, 27, 1969, (1992).

9. S. Bazhenov, J.X. Li, A. Hiltner, E. Baer, "Ductility of Filled Polymers", (Paper in Progress; unpublished).

D. List of All Participating Scientific Personnel

1. Professor E. Baer
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